

### 3.1.6 Trans-DCE

Throughout ISB operations, trans-DCE has appeared recalcitrant to degradation relative to the other chloroethenes. Generally during this reporting period, the trans-DCE concentrations in the source area and outside well TAN-D2 appeared to be decreasing, while trans-DCE in the downgradient, deep, and other outside locations remained fairly constant. For example, trans-DCE at TSF-05A dropped from 437.5 µg/L on October 7, 2002, to 269.1 µg/L on October 6, 2003. Likewise, concentrations of trans-DCE have dropped in TSF-05B from 349.8 µg/L on October 8, 2002, to 292.7 µg/L on October 7, 2003. A decrease was also observed at TAN-25, with trans-DCE concentrations dropping from 208.4 to 182.1 µg/L during the reporting period. Trans-DCE concentrations at TAN-31, however, have remained steady during this reporting period, with concentrations at approximately 250 µg/L. Historical trends in trans-DCE concentrations at TAN-31, however, are decreasing, as trans-DCE peaked during the June 5, 2001, sampling at 510.9 µg/L and has since declined to the much lower concentrations observed during this reporting period. Downgradient and outside trans-DCE concentrations also remained reasonably steady with trans-DCE concentrations at TAN-37 and TAN-29 at approximately 100 to 150 µg/L. Trans-DCE concentrations at TAN-30A remained at approximately 50 µg/L. TAN-D2 appears to have the most responsive trans-DCE concentrations correlating to injection strategy. During the 4X 3% injections, a dramatic increase in trans-DCE concentrations was observed, with the highest concentration of 141.3 µg/L observed on October 7, 2002. These concentrations have since steadily declined to 19.7 µg/L at the end of the reporting period.

## 3.2 Water Quality Monitoring

During this reporting period, multiparameter water quality instruments were deployed in source area wells TAN-25 and TAN-31 and in downgradient wells TAN-37 (A and B depths), TAN-28, and TAN-30A. Results of data collection and operational issues are presented below. In the source area wells, spikes in specific conductance showed the distribution of the sodium lactate electron donor solution following each injection in TSF-05. Following each increase, specific conductance values gradually decreased until the next sodium lactate injection. Temperature, pH, and ORP data were used to assess the aquifer conditions for ARD in the source area.

In situ monitoring at TAN-31 was limited because of equipment issues and construction activities. As a result of those issues, only one injection event (4X 3% injection [February 26, 2003, to February 28, 2003]) was monitored from this location. Conductivity spiked at this well in response to each day's injection activities. In addition, pH and ORP increased during the injection activities. Following the injection, conductivity gradually decreased along with a corresponding decrease in pH and ORP.

Changes in response to injection activities were also monitored at downgradient monitoring locations (TAN-37A, TAN-37B, TAN-28, and TAN-30A), including spikes in conductivity, changes in water level, and drops in pH and ORP (all data provided in Appendix D). The ORP sensors in the instruments deployed at these locations frequently malfunctioned. For instance, most of the ORP data collected from TAN-30A, TAN-37A, and TAN-37B were less than -300 mV. Contrary to this, other redox parameters measured at these locations, including sulfate, iron, and methane, indicate that none of these locations are methanogenic, which is suggested by the extremely low ORP values. Data collected from TAN-28 suggest ORP values of approximately 50 to 100 mV. Changes in ORP as a result of electron donor injection, however, were not observed.

Unlike the ORP data from the downgradient wells, conductivity, pH, and temperature data were more consistent with expected results. Conductivity spikes were observed at downgradient monitoring location TAN-37B, which are likely the result of the flux of higher conductivity water from the residual source area during a 4X 3% electron donor injection. Ambient conductivity at TAN-37B was approximately 1.15 mS/cm, which increased to approximately 1.45 mS/cm during an injection. Unlike TAN-37B, however, other downgradient monitoring locations (i.e., TAN-37A, TAN-28, and TAN-30A) had no change in conductivity that correlated to the electron donor injection. Typical conductivity values for TAN-37A ranged from 0.8 to 1.2 mS/cm, and conductivity values for TAN-28 and TAN-30A were slightly lower with a typical range of 0.80 to 1.0 mS/cm. Also, unlike the source area wells, changes in pH and temperature values could not be correlated to electron donor injections. Aquifer conditions in the downgradient wells show lower temperatures than TAN-31, ranging from 12.7 to 13.2°C, and pH ranging from 6.9 to 7.6.

### 3.3 Water Level Monitoring

Figure 3-41 shows peak observed water level mounding for TSF-05, TAN-25, and TAN-31 from March 1999 through September 2003. Prior to January 2002, the data logger time step was 2 hours. Following the January 2002 injection, the data logger time step was 5 minutes; 10 minutes following the March 2002 injection; and 15 minutes following the October 2002 injection until after the February 2003 injection. Water level data were collected every 4 hours at TAN-25 following the April through September 2003 injections. The longer time steps are not sufficient to record accurate peak mounding following an injection but may be used to estimate mounding changes occurring during this period. Change in injection volumes and rates that may affect the mounding response are also shown in Figure 3-41.

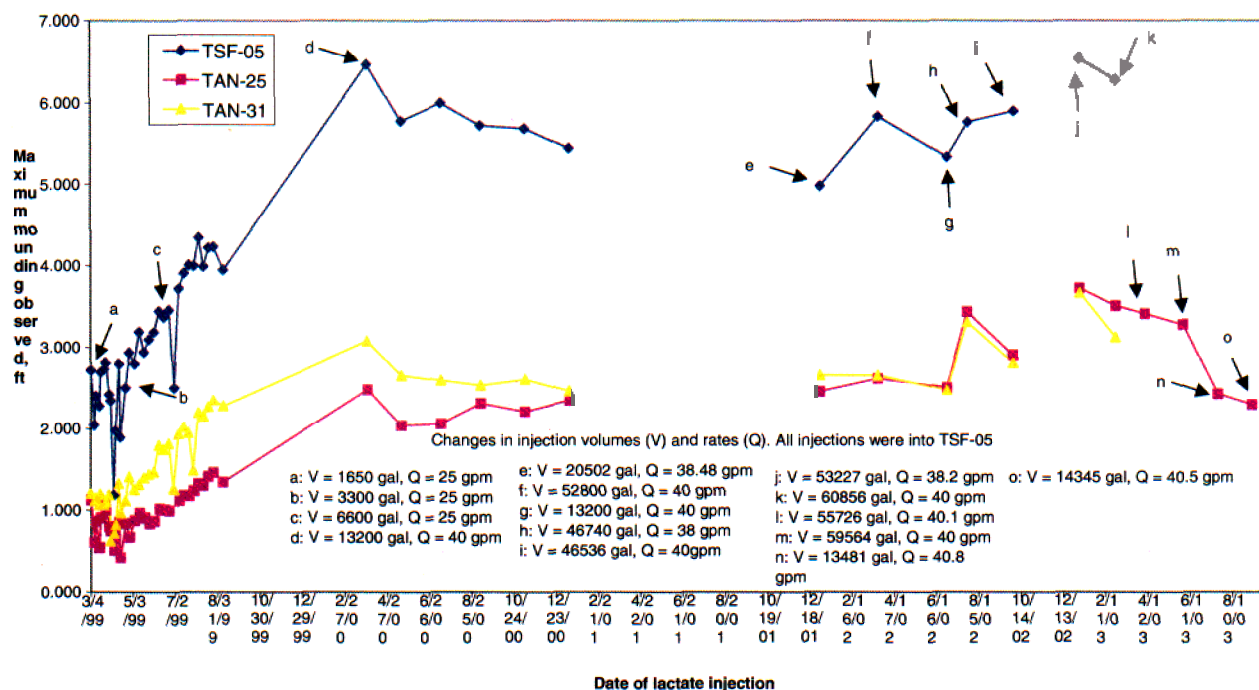


Figure 3-41. Peak water level mounding following sodium lactate injections.

As shown in Figure 3-41, mounding at TSF-05 has increased from approximately 2.5 ft in early 1999 to greater than 6 ft during January and February 2003 injections. Mounding at TAN-25 and TAN-31 has also increased to over 3 ft. These increases in peak mounding are most likely the result of flow rate, which increased from 25 to approximately 40 gpm. Water level data at TAN-25 show mounding decreases after the June 2003 injection (data points “n” and “o”). This decrease may be due to the smaller volumes injected during July and September 2003.

The relative differences in peak mounding between TAN-25 and TAN-31 have changed over time. During the field evaluation, the peak mounding observed in TAN-31 was 0.5 to 0.75 ft greater than that observed in TAN-25. This difference began to decrease during PDP-II, and the peak mounding values observed at TAN-25 and TAN-31 beginning in January 2001 were very similar. After the February 2003 injection, peak mounding in TAN-25 was 0.4 ft greater than that observed in TAN-31. The decreased mounding in TAN-31 compared to TAN-25 may be the result of an increase in the effective porosity along the flow path from TSF-05 to TAN-31.

### **3.4 Radiological Monitoring**

The ISB 2001 and 2002 Annual Reports (INEEL 2002a; 2003a) concluded that although radionuclides were being mobilized in the vicinity of the TSF-05 in response to amendment injections, concentrations were being rapidly attenuated so that areas downgradient of the ISB treatment cell were not substantially affected. The monitoring requirement for Sr-90 and gamma emitters (Cs-137) was reduced to collection of quarterly samples from TAN-29. Tritium was still to be monitored at all well locations on a monthly basis since tritium data can be indicative of changes in source release rates or other hydrogeologic changes.

Sr-90 concentrations at TAN-29 have shown some variability over the past several reporting periods (Figure 3-42). During the last three quarters of this reporting period, Sr-90 concentrations were in the 50- to 60-pCi/L range, which is comparable to concentrations observed during 2001 and 2002. However, two samples (collected in August and November 2002) exhibited concentrations that were an order of magnitude lower (4 and 13 pCi/L). These values were the lowest recorded at this location. These low Sr-90 values were first observed 5 months after the start of the 4X lactate injection. However, Sr-concentrations returned to previous levels in less than 6 months, approximately halfway through the 4X injection phase. The relative changes in Sr-90 concentrations, in response to the ISB injections, are discussed further in Section 4.5.

Tritium data were collected on a monthly basis during this reporting period for all ISB wells. All tritium data collected during the reporting period are presented in Appendix D (see attached CD-ROM). Tritium concentrations throughout the ISB treatment cell were all below MCL values and thus were not a regulatory concern. However, tritium has proven to be a valuable tracer to help understand plume dynamics over previous phases of the ISB project. Figure 3-43 presents tritium data for downgradient wells TAN-26, TAN-28, TAN-37B, TAN-30A, and TAN-29. As can be seen in this figure, these data exhibited significant variability. Concentration changes of 500 pCi/L between monthly sampling events were not uncommon. In addition, inherent uncertainty in the radiological measurement makes correlation difficult with this data set. (Figure 3-43 includes error bars for TAN-26 data as an example of the uncertainty associated with the tritium measurements.) Nevertheless, with the exception of TAN-28, tritium concentrations at these locations appear to be decreasing when averaged over the past 5 years.

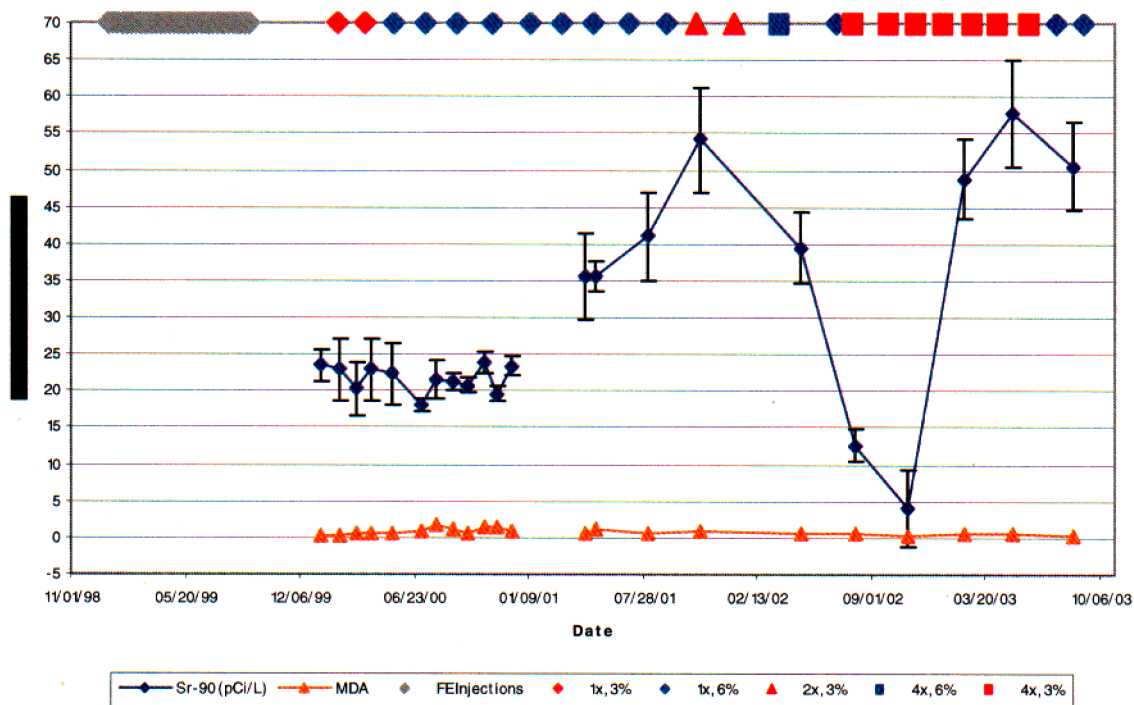


Figure 3-42. Sr-90 concentrations at TAN-29.

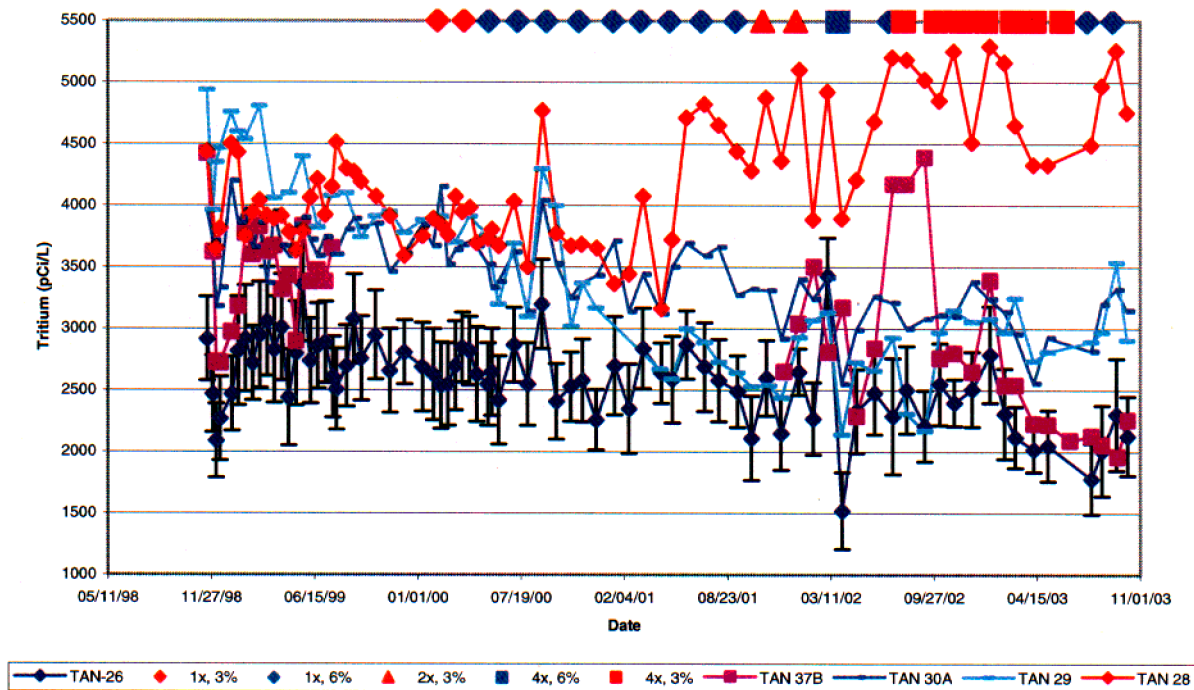


Figure 3-43. Tritium concentrations at in situ bioremediation downgradient wells.

Figure 3-44 presents trends for the tritium data from downgradient wells TAN-28, TAN-37, TAN-30A, and TAN-29. Although the data are not well fit by linear regression due to the variability and inherent error in the data ( $R^2$  values ranged from 0.3 to 0.6 for this data set), concentrations at TAN-37, TAN-30A, and TAN-29 were approximately 1,000 pCi/L less at the end of the 2003 reporting period than when monitoring began in 1999. A hypothetical line corresponding to the natural rate of radioactive decay is also plotted in Figure 3-44 for comparative purposes. The actual tritium degradation constants observed at these locations range from  $1.4 \times 10^{-4}$  to  $2.9 \times 10^{-4}$ . These rates are comparable to the tritium radioactive decay constant ( $1.54 \times 10^{-4}$ ). The minor deviations from this value are likely attributable to heterogeneity in hydraulic conditions and source distribution and release rates. Tritium at TAN-28 exhibited a similar rate of decline from the start of routine monitoring in 1999 through April 2001. By June 2001, however, tritium at this location had jumped to over 4,700 pCi/L and from Figure 3-43, appears to be steady or increasing slightly. This abrupt change, and a similar change in TCE concentration at this location, appears to be an anomaly and is discussed further in Section 4.5.

Figure 3-45 presents a similar trend analysis for the source area wells TSF-05A, TSF-05B, TAN-25, and TAN-26. In this figure, TSF-05A, and TAN-26 decline over time with an observed decay rate constant comparable to the radioactive decay rate for tritium. The relatively rapid decay rate observed in TSF-05B and the slow decay rate observed in TAN-25 are likely the result of injected water diluting the tritium concentrations at TSF-05 and moving relatively contaminated water downgradient towards the TAN-25 location.

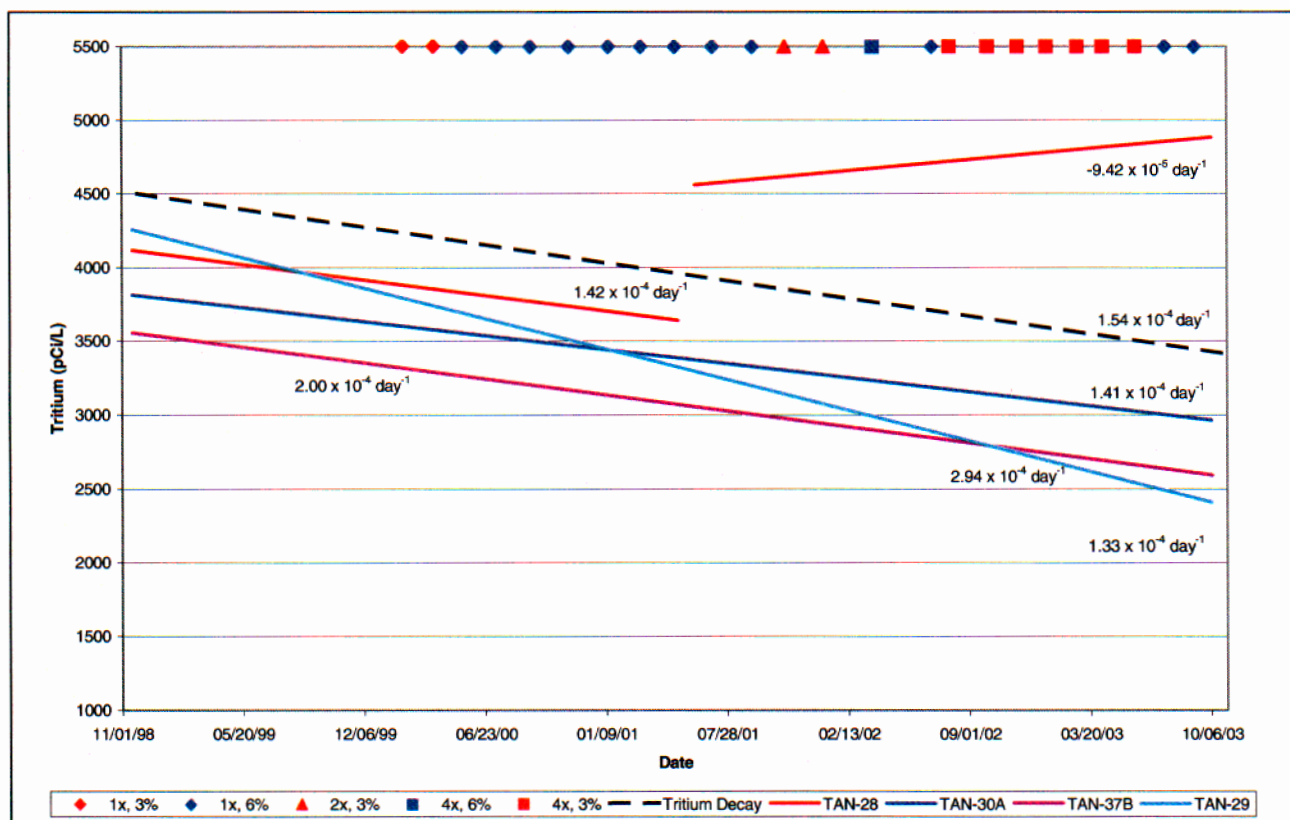


Figure 3-44. Tritium trends at in situ bioremediation downgradient wells.



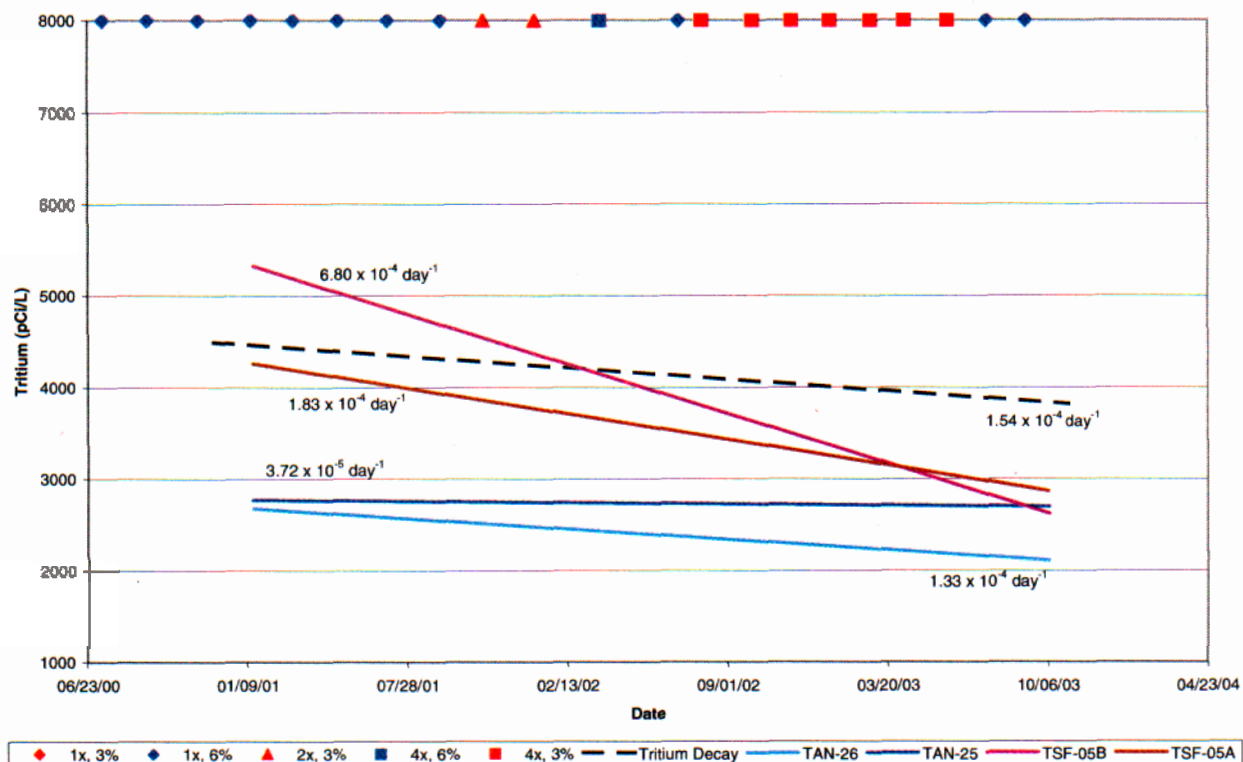


Figure 3-45. Tritium trends at in situ bioremediation source area wells.

In addition to long-term trends in tritium, it is also useful to examine short-term fluctuations that may be indicative of changes in radiological release rates resulting from varying injection strategies. Figure 3-46 shows this period's tritium data for TSF-05 (depths A and B) and TAN-25 and TAN-26, which are the two wells nearest TSF-05 in the downgradient direction. In general, tritium concentrations show a marked drop following each 4X injection with short rebound periods (less than 1 month). At TAN-26, changes in concentrations are not clearly correlated with individual injection events but are relatively constant in the range of approximately 2,000 to 2,500 pCi/L. This is not unexpected since injections of relatively low concentrations of lactate (3 to 6%) do not influence TAN-26.

Gamma emitters were also monitored at TAN-29 during this reporting period. Cs-137 and U-235 values fell below the minimum detectable activity (approximately 4 pCi/L Cs-137 and 23 pCi/L U-235) during this reporting period. All gamma spectroscopy data are provided in Appendix D.

### 3.5 Data Quality Assurance

Monitoring during this phase was conducted primarily to support development of sodium lactate injection strategies and to contribute to the growing set of performance monitoring data. For this phase of operations, the GWMP (INEEL 2002c) required screening level data with semiannual definitive confirmation for VOCs, definitive level data for radionuclides, and screening level data for all other analytes. The QA results from this reporting period indicate that the monitoring data meet the applicable quality requirements. Three distinct sets of QA requirements are specified in the GWMP for the field laboratory analyses, IRC laboratory analyses, and off-Site laboratory analyses. The results of the QA analyses for each laboratory are reported in the respective sections below. The QA sample data are provided in Appendix E.

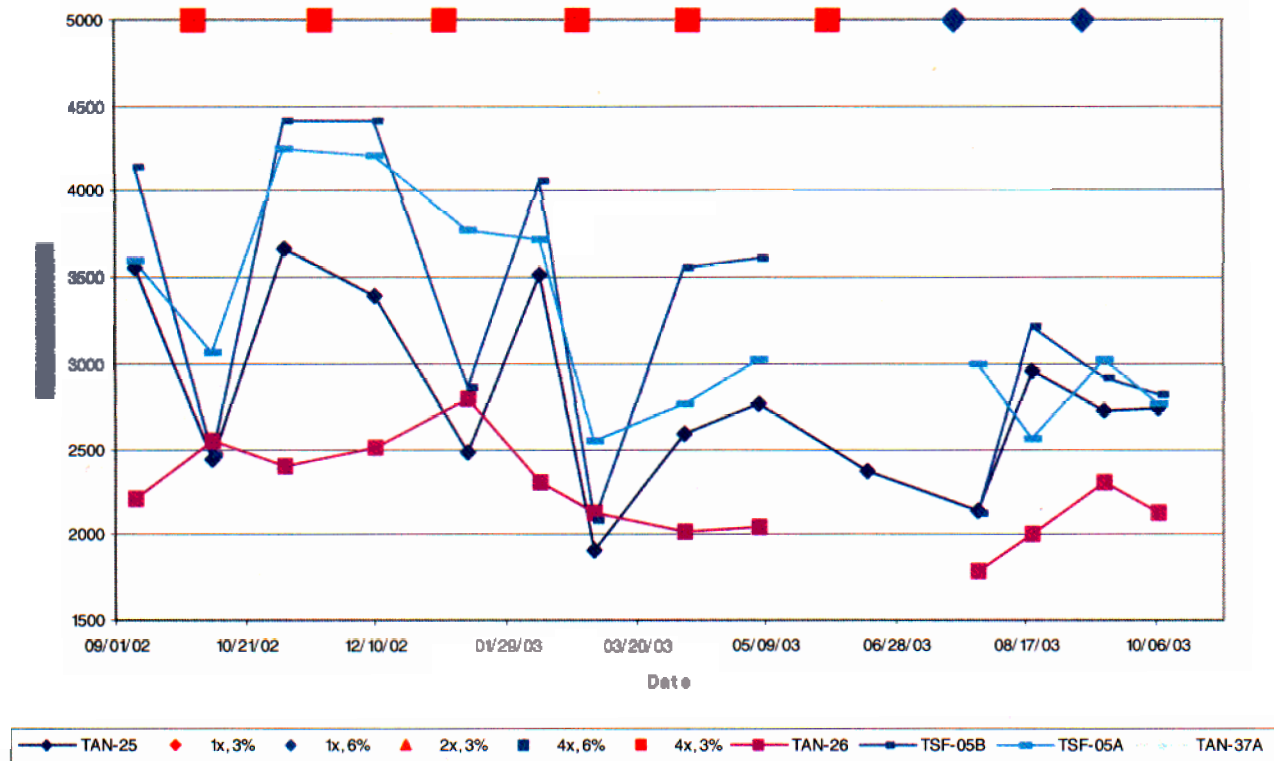


Figure 3-46. Tritium concentrations at locations near the TSF-05 injection well.

**3.5.1.1 In Situ Bioremediation Field Laboratory.** Data generated by the ISB field laboratory are considered screening level data and are used as general indicators of changing geochemical conditions. Therefore, although QA samples are required to be collected and analyzed at a specified frequency, the associated targets for accuracy or precision are established in TPR-166, "In Situ Bioremediation Field Analyses Procedures," as an internal quality check. Definitive data are not required for the ISB field laboratory tests.

Geochemical parameters and nutrients were analyzed immediately after sample collection in the ISB field lab using commercially available field test kits. The GWMP (INEEL 2002c) requires analysis of field duplicates, field blanks, standards, and standard additions (matrix spikes). Acceptable precision and accuracy targets are included in the field laboratory TPR-166. The results of these evaluations indicate that the field tests provide accurate and precise measurements. All COD and alkalinity standard recoveries fell within the ranges specified in the procedure (90 to 110% COD; 75 to 125% alkalinity). Iron standard recoveries were within range (75 to 125%) for 20 of 23 tests. Sulfate was within range (90 to 110%) for 32 of 36 tests. Standard addition tests (matrix spikes) also fell within range (75 to 125%) for all samples and analytes. The field test analyses also proved to be repeatable with duplicate results ranging from 0 to 12% relative percent differences (RPDs) for the majority of samples tested. With the exception of one ferrous iron test, all duplicate results for all of the field test analytes met the target RPD of 25% established in TPR-166. There was no blank contamination found during this reporting period.

**3.5.1.2 INEEL Research Center Laboratory.** The second set of quality requirements pertain to analyses of VOCs, dissolved gas, and electron donor constituents by the IRC laboratory. These data are also considered screening level data where rapid turnaround times and economical analyses are an important consideration. The GWMP requires field duplicates and blanks and also requires the laboratory to perform initial and continuing calibration checks and analyze matrix spike and matrix spike duplicates

(MS/MSDs). The GWMP did not require that specific targets for accuracy and precision be met<sup>a</sup>. As with the ISB field laboratory, IRC laboratory analyses are not required to produce definitive data.

During this reporting period, split samples from each well were sent to the off-Site laboratory on a quarterly basis to address the GWMP requirement for independent verification of the IRC VOC results. As had been reported in previous years, the results of split samples analyzed off-Site by Method 8260B (EPA 1996a) were significantly different than the results obtained using the SPME method at the IRC. With the exception of trans-DCE, the majority of the VOC and dissolved gas split samples had relative differences exceeding 25%. The results of the SPME analysis were both above and below the 8260B results; there was no apparent bias. Details of the split sample analysis are presented in Appendix E.

Because the differences between split sample results could be attributed to a number of factors, a more definitive measure of accuracy of the IRC laboratory methods is provided by using performance evaluation (PE) samples. On a monthly basis, commercially supplied, certified PE standards were included with the groundwater samples submitted to the IRC laboratory. Both high (>100 ppb) and low (<100 ppb) concentration standards were used to evaluate method accuracy in dissimilar concentration ranges. For TCE, cis-DCE, and trans-DCE, all 12 PE results fell within the acceptance ranges. Low-range PCE and high-range VC results were also within range. The only PE samples that were problematic were the low-range VC and high-range PCE. Eight out of 12 low-range VC results fell slightly above acceptance ranges, indicating a possible high bias for VC. Although PE testing should be continued to better understand method accuracy for VC, the data are adequate for monitoring performance trends. It should also be noted that VC is above the MCL only at a few source area wells. Three out of seven high-range PCE results fell below the acceptance ranges. However, high-range PCE recoveries are not critical to the project, as PCE concentrations are very low in the ISB wells. The results of the PE sampling program indicate that the SPME method used at the IRC is reporting VOC concentrations within the specified accuracy range for analytes of interest.

Precision of the VOC and dissolved gas data was also evaluated by comparing results of duplicate samples. The RPD for TCE ranged from 1 to 13%, which met the precision requirement in the GWMP (14%) (INEEL 2003b). The RPD for all other VOC samples ranged from 1 to 21%, with the majority of the duplicate samples falling within 10% of each other. Dissolved gas results were not as precise. Ethene RPD ranged up to 52%, with one methane pair showing a 151% difference. Ethane could not be evaluated, as all duplicate sample results were below the detection limit. Because dissolved gasses are used as a qualitative indicator of geochemical conditions, there is no precision or accuracy limit required for these analyses.

**3.5.1.3 Off-Site Laboratories.** The third set of quality requirements apply to analyses conducted by “off-Site” commercial laboratories. Off-Site laboratories are used for gamma spectroscopy and gross alpha analyses. The GWMP also specifies that split samples be sent semiannually to off-Site laboratories for definitive confirmation of VOC concentrations by SW-846 Method 6010B, “Inductively Coupled Plasma-Atomic Emission Spectrometry” (EPA 1996b). The GWMP invokes definitive data requirements for all off-Site laboratories according to the INEEL *Quality Assurance Project Plan for Waste Area Groups 1, 2, 3, 4, 5, 6, 7, 10, and Inactive Sites* (DOE-ID 2002c). The required QA samples include duplicate samples, standards, and matrix spikes. Specific acceptance ranges for duplicates, standards, and matrix spikes are specified for TCE only.

All off-Site TCE duplicate samples met the target RPD of 14%. For the remaining VOC analytes, the RPD ranged from 0 to 18%. Tritium and Sr-90 duplicate sample results ranged from 0 to 23% with one outlying tritium result at 71% RPD. As mentioned previously, a target precision value is only specified for TCE. Standard and matrix spike recoveries were evaluated as part of the Level A data validation. Standard

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a. A subsequent revision (Rev 2, December 2003) (INEEL 2003c) of the GWMP, as used throughout the remainder of this report, requires that precision and accuracy targets be established in the Scope of Work for the IRC laboratory.



sample recoveries fell within range for all VOC analyses. Matrix spike/matrix spike duplicate sample recoveries fell within range for all PCE and TCE analyses, but only two of the four VC analyses were within range. Less than half of the dissolved gas MS/MSD samples were within range. In addition to the laboratory prepared spikes, two commercially prepared PE samples were also submitted to the off-Site laboratory for VOC analysis in May and August 2003. The May sample was a low value (<100 µg/L) VOC sample and results for all analytes were within range. The August sample was a high value (>100 µg/L) VOC sample and while TCE, PCE, and VC were within range, cis-DCE and trans-DCE results were biased high.

### 3.6 Microcosm Studies Results

Microcosm studies designed to test the degradability of trans-DCE relative to cis-DCE and TCE were conducted as part of Fiscal Year 2003 TAN ISB operations. Residual trans-DCE in the field at TAN has spurred questions regarding whether trans-DCE is actually biodegrading anaerobically. A laboratory TCE-dechlorinating community enriched from TAN-25 groundwater (Wood, Cummings, and Sorenson 2002) was used to inoculate three microcosms, as described in Section 2.7. This culture readily degraded both cis-DCE and TCE but not trans-DCE. Trans-DCE actually appeared to inhibit cis-DCE and TCE dechlorination. In the microcosms amended with only TCE and cis-DCE, the culture readily degraded both constituents to ethene within 1 month (Figures 3-47 and 3-48). The culture amended with trans-DCE, however, was incapable of degrading this contaminant and the presence of trans-DCE actually appeared to inhibit the degradation of the residual TCE and cis-DCE initially present in the microcosm (Figure 3-49). The trans-DCE microcosm was again sampled after 3 months and TCE and cis-DCE appeared to have been degraded; however, trans-DCE was not. Some ethene production is evident in Figure 3-49, though it is likely that it was produced by the dechlorination of the TCE and cis-DCE present in the microcosm and not from degradation of the trans-DCE. The reductions in trans-DCE observed were likely a result of a loss to the system, as reductive daughter products were not observed.

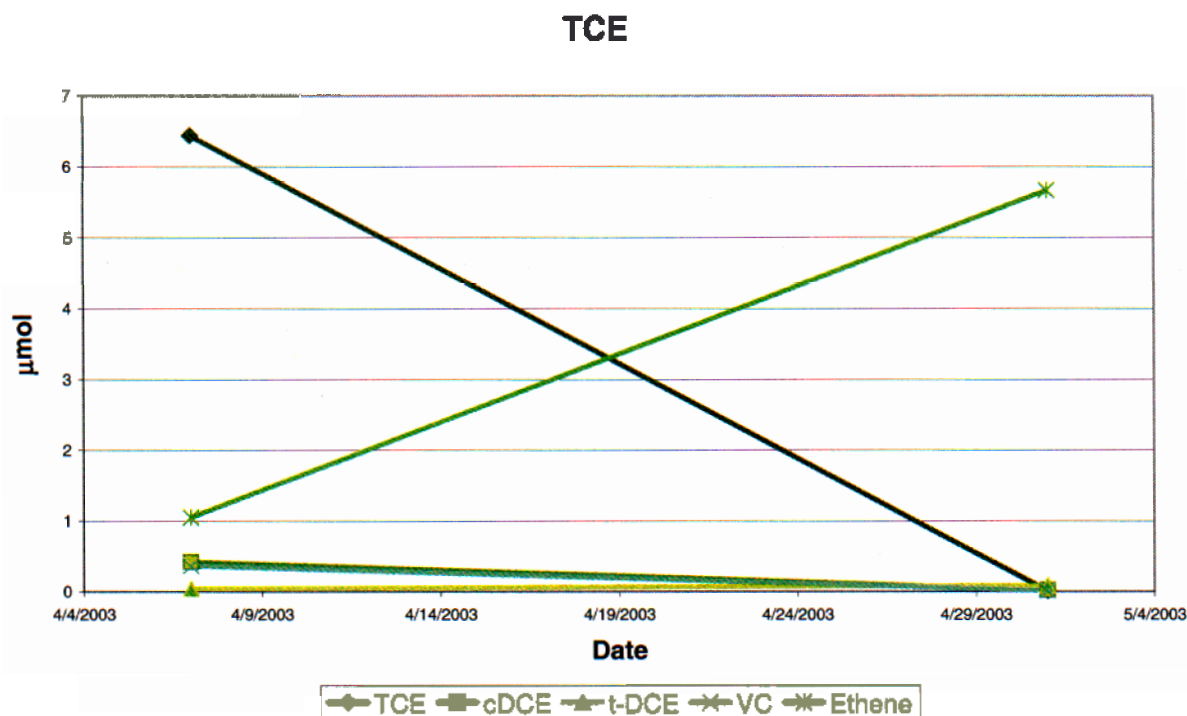


Figure 3-47. Results for microcosm amended with TCE.

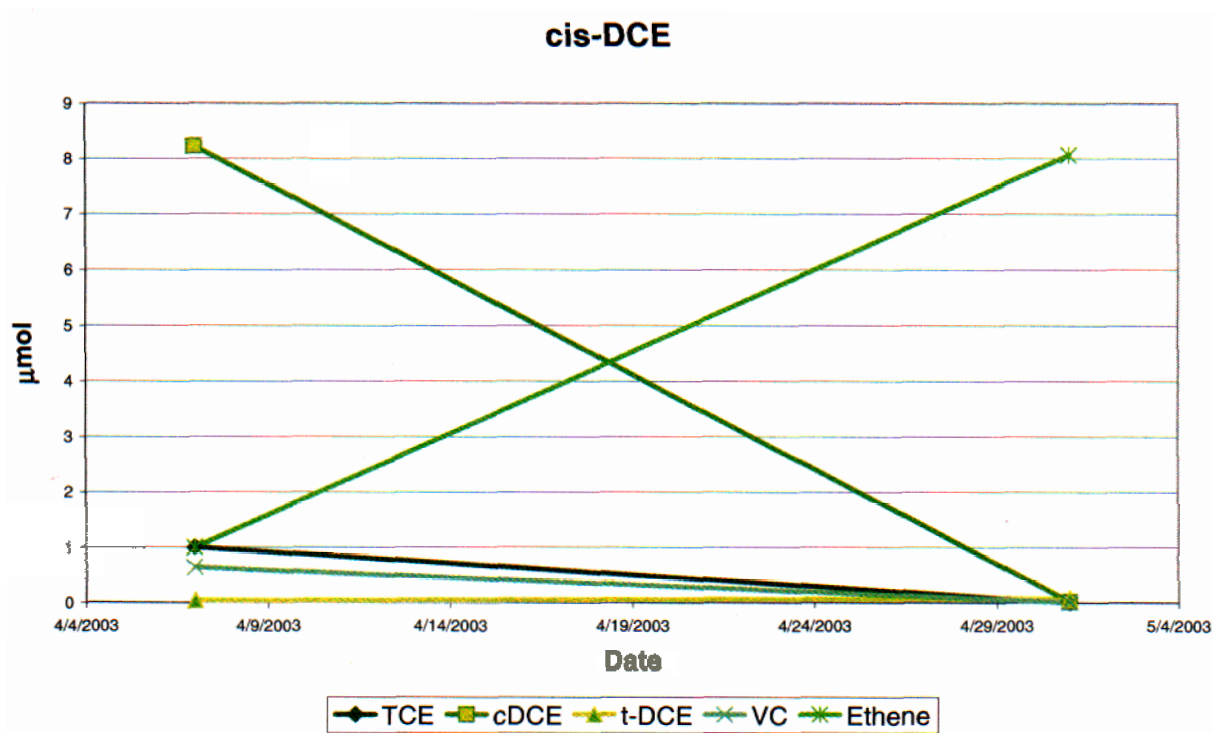


Figure 3-48. Results for microcosm amended with cis-DCE.

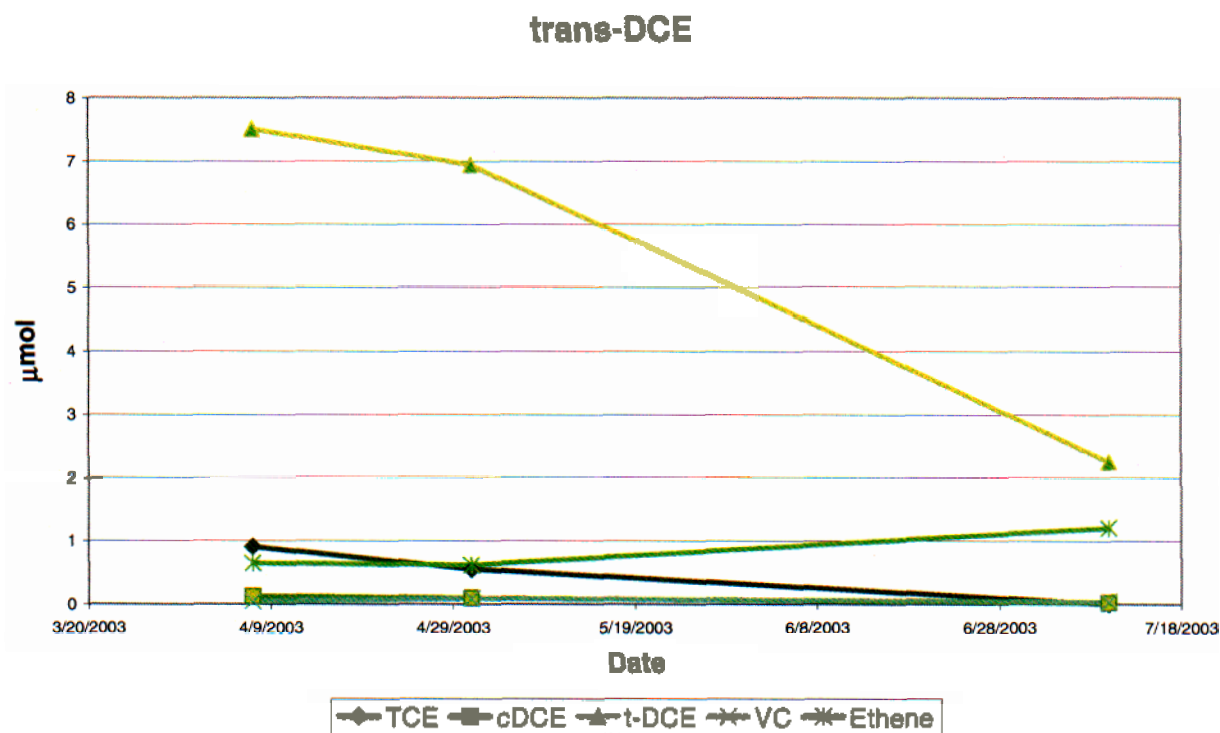


Figure 3-49. Results for microcosm amended with trans-DCE.



## **4. DISCUSSION**

This section discusses the results from the reporting period in the context of the overall effectiveness of the ISB remedy. Section 4.1 discusses the effectiveness of ISB operations, including distribution and utilization of electron donor. Section 4.2 discusses characterization of the new wells, TAN-1859, TAN-1860, and TAN-1861. Section 4.3 discusses impact of ISB on the source, including recent data verifying the conceptual model of the secondary source term and evidence of source destruction in the area near monitoring well TAN-D2. Section 4.4 discusses recent radiological and VOC trends at TAN-28. Section 4.5 discusses effects of injection on radionuclide migration, and Section 4.6 briefly presents several options for additional cost efficiencies.

### **4.1 Operational Effectiveness**

This section discusses the results of groundwater monitoring in relation to electron donor distribution, utilization, and ARD efficiency.

#### **4.1.1 Electron Donor Distribution**

During the current reporting period, testing of alternate injection strategies continued with the goal of encompassing the entire residual source area using a single injection well, TSF-05. As presented in Section 3, high volume, low concentration (4X 3%) injections were performed through June 2003 in an attempt to create the appropriate distribution of electron donor. The 4X 3% injections maintained extremely reducing conditions appropriate for ARD of TCE to ethene in the source area wells. Little to no electron donor was observed at deep wells TAN-26 and TAN-37C, suggesting that the low injected lactate concentrations also minimized vertical transport. Beneficial trends, such as more reducing redox conditions and decreases in TCE with concurrent increases in ARD daughter products, were observed near the outer boundaries of the source area. For example, at TAN-37, TCE concentrations decreased temporarily in March and April 2003 and cis-DCE concentrations increased coincident with the onset of sulfate and iron reduction. TAN-D2, near the upgradient edge of the source area, also exhibited decreases in VOC concentration and reducing geochemical conditions. This suggested that the 4X 3% injections may have been successful in distributing electron donor near the outer edges of the residual source. However, by June 2003, TCE concentrations and redox conditions had returned to near pre-4X injection levels at TAN-37, suggesting the initial distribution of electron donor attained with the 4X injections was diminishing over time.

#### **4.1.2 Electron Donor Utilization**

In addition to electron donor distribution, the optimization process includes an analysis of the amendment utilization rate, which may dictate the frequency of electron donor injections in the field. The goal of this process is to minimize the frequency of electron donor injections while maintaining a relatively high rate of dechlorination. By examining utilization of lactate and total electron donor as COD for well locations after each of the electron donor injections, correlations can be made between electron donor utilization and distribution. Detailed analysis of the first order degradation rate coefficients for lactate and COD was presented in Section 3.1.2 for several source area wells. The conclusion was that the degradation rates were correlated to concentration and distribution of electron donor. In general, the low volume, high concentration injections (1X 6%) resulted in increased utilization near the injection point (wells TSF-05 and TAN-25) but decreased utilization farther crossgradient (TAN-31) due to the low amount of electron donor that was distributed to this location. Conversely, the high volume, low concentration (4X 3%) injections resulted in lower utilization near the injection point (TSF-05 and TAN-25) but higher utilization at TAN-31 due to increased distribution of electron donor to this location. The higher utilization at TAN-25 during 1X 6% injections did not correlate to higher donor concentrations. In fact, the highest utilization was observed after the 1X injections when much lower concentrations of electron donor were actually reaching TAN-25 than during the 4X injections. In addition, reduction of accumulated cis-DCE at TAN-25 occurred at these increased utilization rates and lower electron donor concentrations.

For well TAN-25, a comparison between historical COD and lactate utilization rates during all 1X 6% injections and 4X 3% injections conducted throughout ISB operations was made to determine differences over time. It has been shown at TAN that the concentration of COD directly correlates to the concentration of total volatile fatty acids, including lactate, acetate, propionate, and butyrate (INEEL 2002a). Therefore, COD utilization is used to interpret total electron donor degradation. Figure 4-1 presents the estimated first order degradation rate constants for COD after each of the injection events from May 2000 to present. The rate constants are divided into three groups: (1) the original 1X 6% injections conducted during May 2000 until October 2001; (2) the 4X 3% injections conducted between November of 2001 and June 2002; and (3) the 1X 6% injections conducted from July 2003 to present.

In Figure 4-1, the observed degradation (utilization) coefficients are also fitted by a linear regression for the first two injection strategies to illustrate the increasing trend. During the first period, nine lactate injections (1X 6%) were made and the COD degradation coefficient doubled during the injection period (from 0.05 to 0.10). This is consistent with growth-phase microbial use where biomass is increasing in the system. During the period between the first set of 1X 6% injections and the 4X 3% injections, several different injections strategies were employed (INEEL 2002a). The second injection period (4X 3%) began with a COD utilization rate (0.09) comparable to the utilization rates observed at the end of the first period; over the next six injections the utilization rate increased to 0.12. The COD utilization coefficients observed during the third period (the recent 1X 6% injections) are the highest utilization rates of any observed. These data suggest that the COD utilization rate is generally increasing over time, independent of the electron donor injection strategy.

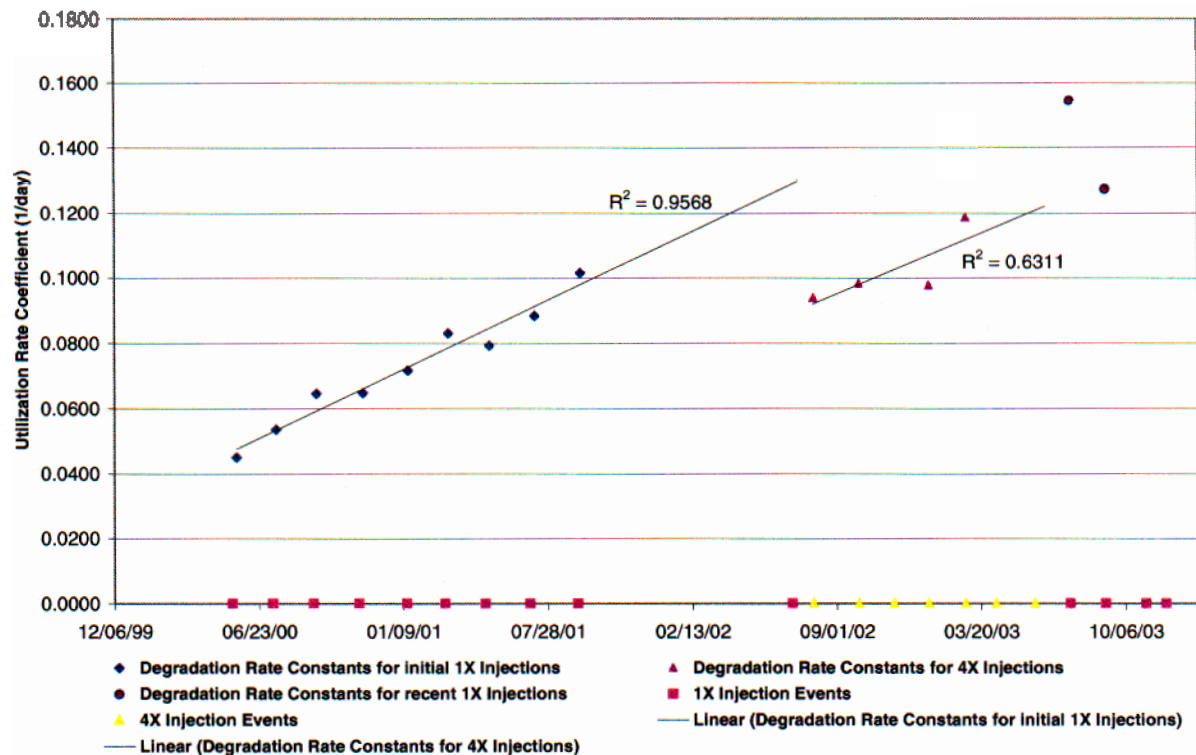


Figure 4-1. Estimated first order degradation rate constants for chemical oxygen demand after each of the injection events from May 2000 to present at TAN-25.



In contrast to COD, no strong evidence for an overall trend in the lactate degradation rate coefficients across the three different injection strategies was observed (Figure 4-2). The lactate degradation rate coefficients were relatively similar both within and between groups. The average for the first group (1X 6%) was  $0.27 \pm 0.04^b$ ; the second group (4X 3%) averaged  $0.25 \pm 0.06^b$ ; and the third group was the most different with an average rate of 0.37. It should be noted, however, that the last group had an insufficient number of data points to reliably determine a population mean.

The difference between the increase in COD utilization rate over time versus the relative stability of the lactate utilization rate may be explained biologically. Lactate fermentation is thermodynamically the most favorable reaction under geochemical conditions prevalent at TAN, so it proceeds very quickly. A slight increase in lactate utilization was observed after the two 1X 6% injections, and more stable utilization rates after this suggest that the lactate-fermenting biomass had reached a relative equilibrium. The apparent increase in COD utilization rates, however, could be due to the slow growth of microbial populations that utilize propionate and acetate. After 5 years of amendment injections, it appears that the biomass is still in the growth phase, and as more biomass develops, these electron donors are utilized more rapidly. Additional data collected over the optimization phase should verify whether COD utilization rates continue to increase. At some point, utilization rates may need to be managed through the intermittent use of alternate donors in order to keep the necessary frequency and volume of injections proportional to the rate of dechlorination.

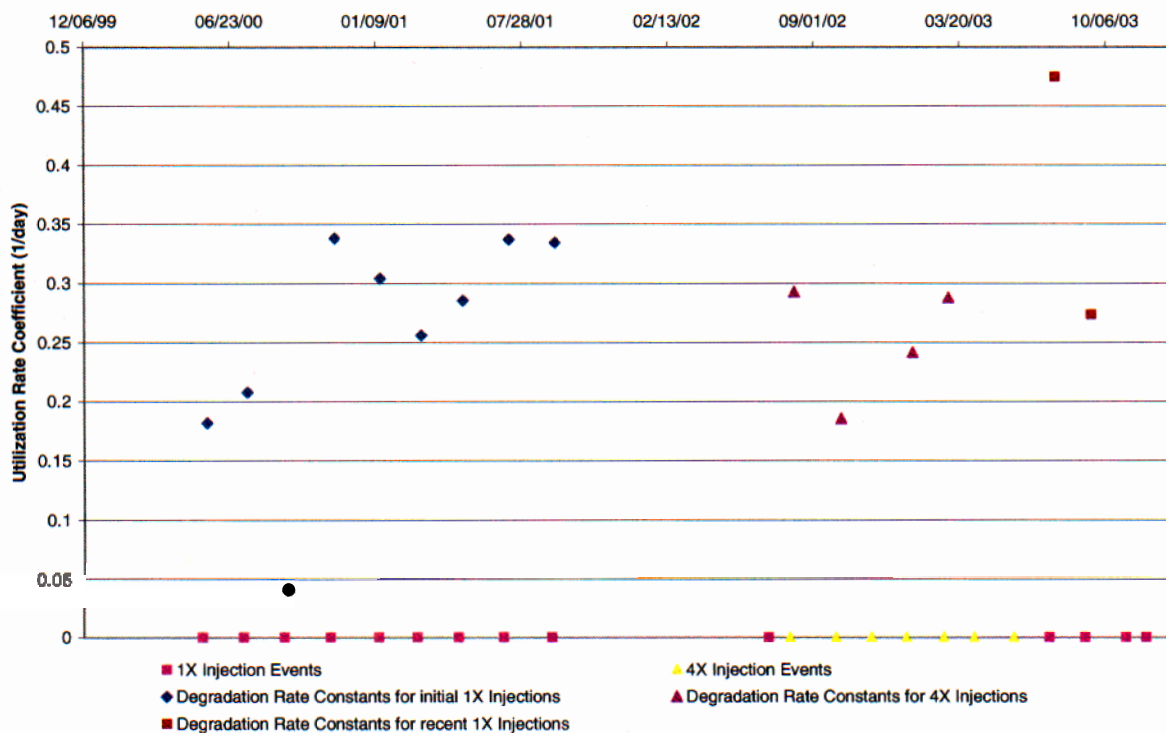


Figure 4-2. Lactate degradation rate coefficients at TAN-25.

b.  $\pm 1$  standard deviation.

#### **4.1.3 Anaerobic Reductive Dechlorination Efficiency**

Significant increases in cis-DCE concentrations (~100 to 300 µg/L) in TAN-25 were observed after each of the 4X injections, and high spikes in cis-DCE concentrations were observed at TAN-31 (~100 to 150 µg/L) after the September 2002 and January 2003 injections but not after the February 2003 injection (17 µg/L). These spikes in cis-DCE are attributed to the negative impact of the aerobic water on the anaerobic microbial community. This suggests that the 4X injections were reducing ARD efficiency near the injection point but that the zone of efficient ARD may have been extended farther away from the injection point because of the increased distribution of electron donor.

As reported in Section 3, VOC concentrations were temporarily impacted at the downgradient wells during the high volume (4X 3%) injections. For example, TCE concentrations at TAN-37A and TAN-37B reached all time lows in the spring of 2003. The dip in TCE was correlated to an increase in cis-DCE and VC. The total chlorine number also dipped at this time, suggesting that active ARD was occurring near these locations (Figures 3-31 and 3-32). TAN-D2 also exhibited significant changes in VOC and redox conditions, which indicated that active ARD was occurring in the upgradient direction as well. The dip in TCE concentrations and total chlorine number suggests that there was reduced contaminant flux from the residual source area at this time.

The temporary increase in ARD observed at TAN-37 and the changes at TAN-D2 indicate that injections at TSF-05 were partially successful at influencing the majority of the source area. However, effective ARD conditions have not been consistently established at TAN-37. It is suspected that increased utilization of donor along the flow path to TAN-37 may be limiting the transmission of electron donor from TSF-05 to that location. Utilization of additional injection points may be necessary to sustain ARD in that portion of the treatment cell.

In addition, because ARD efficiency decreased in the center portion of the source during the 4X 3% injections, alternative injection strategies may be more effective at sustaining ARD conditions. For example, the diminished efficiency of ethene production near the injection point during the 4X 3% injections prompted a decision to revert back to a lower volume, higher concentration 1X 6% injection strategy in July 2003. This resulted in higher concentrations of electron donor at the injection point but decreased distribution of electron donor to downgradient and crossgradient locations. Although electron donor concentrations were lower during the 1X 6% injections, the magnitudes of the injection induced spikes in cis-DCE concentration at TAN-25 and TAN-31 began to decline and are now similar to those observed during the pre-4X 3% injection operations. These data indicate that ARD efficiency near TSF-05 is returning to pre 4X 3% conditions, as desired.

The data generated over the 2003 reporting period indicate that continued testing of injections at TSF-05 and other locations is necessary to fully encompass the residual source sludge area and to arrest contaminant migration to a downgradient location.

#### **4.1.4 Persistence of trans-DCE**

Trans-DCE has persisted in the treatment cell since the onset of ISB operations. In general, concentrations of trans-DCE have remained steady in source area wells and appear to decrease downgradient. As of October 2003, the highest concentration within the treatment cell (around 270 µg/L) was at TSF-05A. TAN-37A and TAN-37B have shown an increase in trans-DCE since the end of the previous reporting period (October 2002); concentrations in October 2003 were around 120 and 130 µg/L, respectively. While concentrations at TAN-28 have recently decreased and have been below 100 µg/L during recent monitoring events, it is too early to conclude whether trans-DCE will remain at low concentrations at this location.

It is thought that the trans-DCE in the treatment cell is a result of its presence as an original contaminant in the secondary source, and possibly as a result of its generation during the biological degradation of TCE. Even though trans-DCE appears relatively recalcitrant to degradation compared to cis-DCE, other attenuation processes (e.g., dispersion) are still sufficient to result in the reduction of concentrations to acceptable levels at the downgradient edge of the ISB treatment cell, as indicated by the results from TAN-29 (Figure 3-38).

Results of the comparative microcosm studies indicated that under controlled conditions, microcosms spiked with TCE and cis-DCE dechlorinated rapidly in accordance with dechlorination rates previously observed. Microcosms spiked with trans-DCE, however, exhibited constant concentrations of trans-DCE over a 1-month period. The data suggest that trans-DCE is being dechlorinated at a much slower rate than TCE and cis-DCE, if at all. In fact, residual concentrations of cis-DCE and TCE were degraded nearly twelve times slower than the same constituents in microcosms that contained no trans-DCE. This suggests that the presence of elevated levels of trans-DCE may be inhibitory to dechlorination of other chloroethenes known to be readily degraded otherwise.

## **4.2 Characterization of the New Wells**

As described in Section 2.4, three new wells (TAN-1859, TAN-1860, and TAN-1861) were drilled during this reporting period. Preliminary sampling results from these wells confirm the conceptual model for the hot spot at TAN in terms of the distribution of residual source material.

### **4.2.1 TAN-1859**

A key component of the revised injection strategy was to complete a second injection well near the downgradient edge of the source term sludge. As stated previously, it was estimated that the sludge extended 30 m (100 ft) from TSF-05, terminating somewhere between TAN-25 and TAN-37. Data developed during well installation and subsequent monitoring indicate that TAN-1859 was drilled just inside the residual source area and completed in the sludge zone. The first line of evidence comes from an examination of the borehole logging data. The caliper log (right panel of Figure 4-3) indicates that the interval between 235 and 240 ft bls is not in solid basalt but appears to be highly fractured or rubbleized. The gamma log (left panel of Figure 4-3) indicates elevated activity in this interval, indicative of waste sludge material. This interval of elevated gamma activity correlates with similar gamma spikes observed at the same intervals (~210 to 220 ft bls) in TAN-9, TAN-31, TSF-05, TAN-25, and TAN-26 (Figure 4-4).

The second line of evidence is that groundwater sampling results at this location show low levels of electron donor (acetate and propionate only). Redox conditions are strongly methanogenic, as evidenced by the elevated ferrous iron concentrations, high methane concentrations, and lack of sulfate (Figures 3-12, 3-16, and 3-20). TCE and c-DCE concentrations range from 20 to 30 µg/L, while trans-DCE has been approximately 230 to 250 µg/L (Figure 3-28). The redox data, along with the low concentrations of TCE and c-DCE, suggest that TAN-1859 is just inside the biologically active zone, the extent of which is smaller than the residual source. Additional confirmation that TAN-1859 was completed in the source sludge was provided during a routine radiation field measurement. Technicians identified elevated radiological activity on paper wipes used to decontaminate sampling equipment removed from TAN-1859. It was suspected that the observed activity was caused by Cs-137 contamination. Because Cs-137 has only been detected reliably in the source sludge and does not persist in the downgradient medial zone area, this observation provides further evidence that TAN-1859 was drilled within the source sludge.

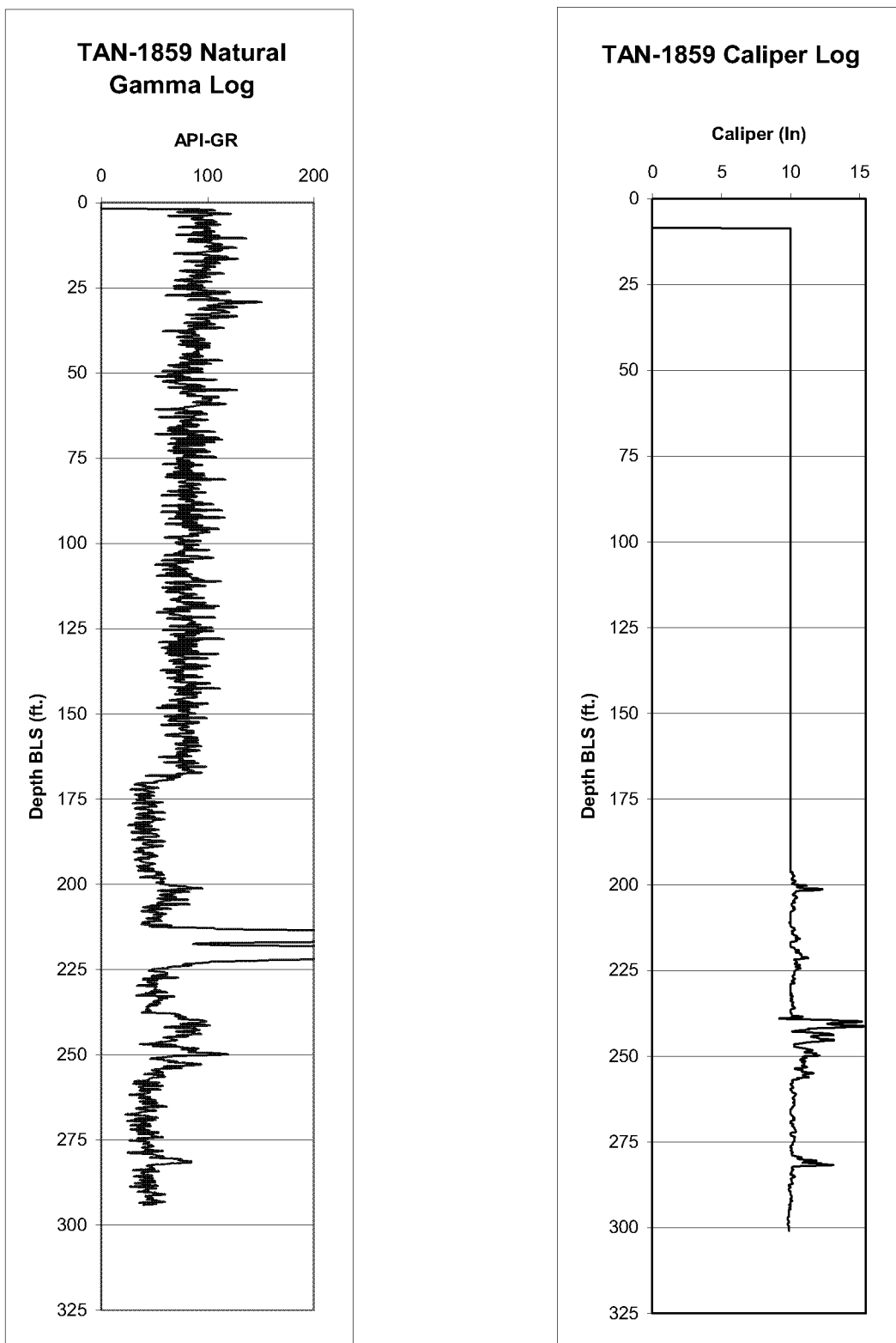


Figure 4-3. Borehole logging data (passive gamma and caliper readings) for TAN-1859.

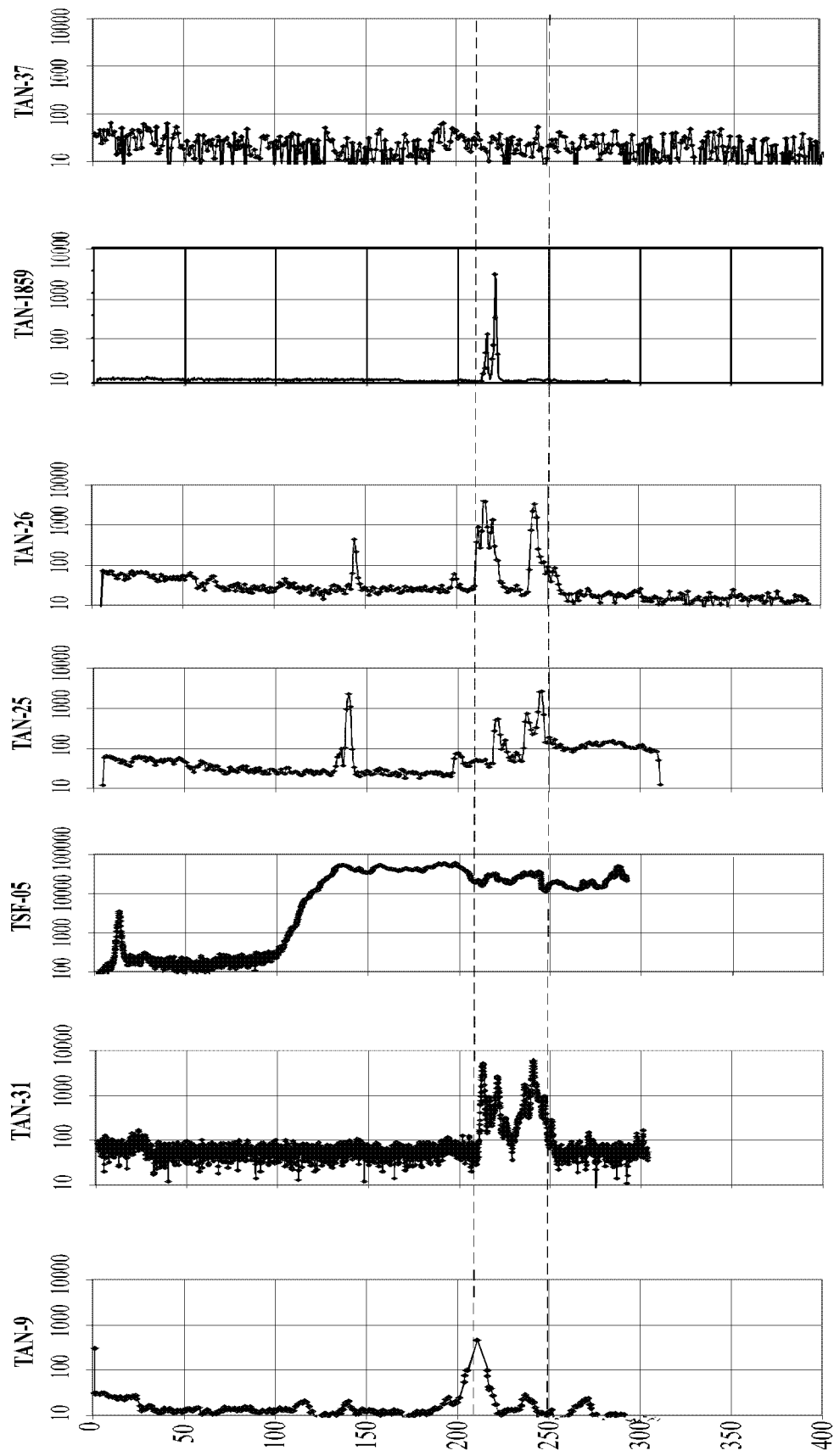


Figure 4-4. Correlation of gamma readings at TAN-9, TAN-31, TSF-05, TAN-25, TAN-26, TAN-1859, and TAN-37.



#### **4.2.2 TAN-1860 and TAN-1861**

TAN-1860 and TAN-1861 were drilled downgradient and crossgradient from TAN-37. These wells were drilled well outside of the residual source area. The primary piece of empirical evidence to support this claim is the natural gamma logs presented in the TAN Well Completion Report (INEEL 2003c). The natural gamma logs showed no spikes to correlate with contaminated sludge found in the source area. This demonstrates, as expected, that there is no source material within TAN-1860 and TAN-1861. TAN-1861, however, did have a small spike from 210 to 212 ft. Upon consulting the lithographic log for this well, this corresponds to a sedimentary interbed (likely the P-Q interbed), which has been encountered in approximately two-thirds of the wells at TAN from 180 to 340 ft bls, ranging in thickness from 1 to 15 ft (INEEL 2000). This spike probably correlates to the higher levels of K-40 concentrations that occur naturally in the sediments.

The geochemistry in these wells also supports that they are located outside of the residual source area. Electron donor has not reached TAN-1860 and TAN-1861 and the observed redox conditions are anaerobic but only mildly reducing, as evidenced by the presence of sulfate and absence of ferrous iron. Elevated methane and TCE concentrations result from transport of upgradient groundwater (Figures 3-14, 3-18, 3-22, 3-33, and 3-36). Anaerobic reductive dechlorination is not actively occurring in these wells and there is no ethene production. These results are consistent with those from nearby axial wells TAN-28 and TAN-30A.

### **4.3 Impact of In Situ Bioremediation on the Source**

This section discusses the observed area of ARD influence in relation to the conceptual model of the residual source area. It also highlights recent evidence of complete source destruction in the vicinity of TAN-D2.

#### **4.3.1 Extents of the Treatment Area and Source Area**

A conceptual model for the OU 1-07B contaminated groundwater plume was developed during the late 1990s using an iterative process of defining data gaps and conducting tests to address specific questions (Sorenson, Wylie, and Wood 1996; Bukowski and Sorenson 1998; Bukowski, Bullock, and Neher 1998; Wymore, Bukowski, and Sorenson 2000). As part of this work, a description of source term and mechanisms of contaminant release was also developed based on analysis of contaminant distributions, geochemical properties, hydraulic testing, and numerical modeling. The resulting conceptual model provides the basis for evaluating the effectiveness of the OU 1-07B remedial action.

Because the hydrogeologic framework of the source area at TAN is characterized by alternating layers of dense basalt flows with relatively porous zones (rubble zones) occurring at the interfaces between basalt flows, there exists a strong preferentially horizontal flow at the scale of the source area. However, it has been demonstrated that the effective porosity of the aquifer has been substantially reduced in the vicinity of TSF-05 due to the presence of the waste sludge (INEEL 1998; Sorenson 2000). These data and other corroborating evidence supported a conceptual model whereby contaminated organic material is entrapped in the basalt matrix creating a significant secondary source in the formation surrounding the TSF-05 injection well. It is estimated that the radius for the sludge distribution around TSF-05 is about 30 m (100 ft) (Sorenson 2000; Wymore, Bukowski, and Sorenson 2000). As groundwater flows through open pore spaces in the residual source area, it becomes contaminated by compounds diffusing out of the sludge. The implication is that even with a biologically active zone being maintained in the vicinity of TSF-05, residual source material further downgradient would continue to release contaminants into the groundwater flowing past this area. This conceptual model explained the concentrations of contaminants observed in past reporting periods at TAN-37A, downgradient of the biologically active zone. This concept was discussed in Sale (1998) and applied specifically to the OU 1-07B conceptual model in Sorenson, Peterson, and Ely (2000).

Figure 4-5, adapted from Sorenson (2000), provides a hypothetical illustration of the secondary source term. Even with active biological activity at TSF-05, crossgradient and downgradient contaminant flux from the source area would be expected to continue when the residual source area is not fully encompassed by the biologically active zone. Figure 4-6 illustrates the desired condition where the entire source area is encompassed by the biologically active zone, effectively cutting off downgradient and crossgradient flux from the source area. It is expected that after a sufficiently large ARD area is established, it can be maintained to reduce the mass of source sludge remaining (Figures 4-7 and 4-8).

Considering the conceptual model for the source term, combined with amendment distribution data, the injection strategies tested during this reporting period did not sustain an active ARD zone large enough to encompass the entire source area. In addition, the 4X injection strategy did not maintain efficient ARD near the injection point. Therefore, revised injection strategies have been developed, including utilization of additional injection wells (TAN-1859 and potentially TAN-31). Other modifications to the injection strategy, such as injecting into the upper portion of the aquifer (i.e., installing packers in the injection wells), may also be considered. Continued optimization of the injection strategies is expected to increase the area of biological activity with the goal of sustaining active ARD throughout the residual source area. Although it is anticipated that a larger fraction of the source term will be impacted by biological activity using two-well injections (as compared to single well injections into TSF-05), it is undetermined whether small pockets of source material at the northern and southern edges may continue to provide a flux of contaminants from the source area. The compliance monitoring wells (TAN-1860 and TAN-1861) that were constructed during this reporting period will provide data to indicate whether a large enough biological activity zone can be created to encompass the outer fringes of the secondary source term.

#### **4.3.2 Source Destruction at TAN-D2**

Previous to this reporting period, all discussions of source degradation were based on indirect measurements such as increased porosities near TSF-05 and lower maximum groundwater mounds observed during lactate injections. During this reporting period, the first evidence of local, complete source degradation from ISB at TAN was observed at TAN-D2. While conditions at TAN-D2 will continue to be monitored to validate the degradation of the residual source, the current data indicate that ISB has degraded the source material at this location and the area near TAN-D2 has been successfully remediated.

As reported in Section 3.1.2.2, though little electron donor was distributed to TAN-D2 during the reporting period, electron donor has been seen at this location in the past. However, the larger 4X 3% injections did result in electron donor distribution near TAN-D2, as evidenced by the onset of methanogenic conditions, which was indicated by reduction of sulfate to 0 mg/L and presence of ferrous iron and methane (Figures 3-15 and 3-19). Concurrently, TCE concentrations declined to nondetect, as shown in Figure 3-36. Currently, the only VOC at TAN-D2 remaining above the detection limit is trans-DCE, which decreased from 118.2 to 19.7 µg/L during this reporting period; the maximum contaminant level for trans-DCE is 100 µg/L. The importance of the trans-DCE trend at TAN-D2 cannot be overstated. Since trans-DCE acts as a tracer for residual source material, the dramatic increase observed in response to the 4X injections indicates that additional source material was contacted by these larger volume injections. The fact that trans-DCE is now significantly declined, combined with the fact that no TCE rebound has occurred and the fact that ethene production at TAN-D2 has ceased, suggests that this source material has been degraded.

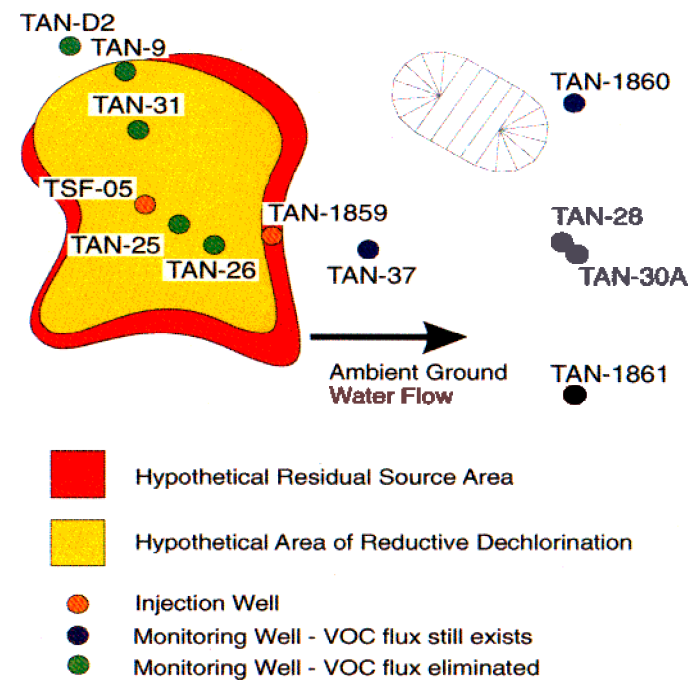


Figure 4-5. Single injection point - residual source extends beyond area of active biodegradation.

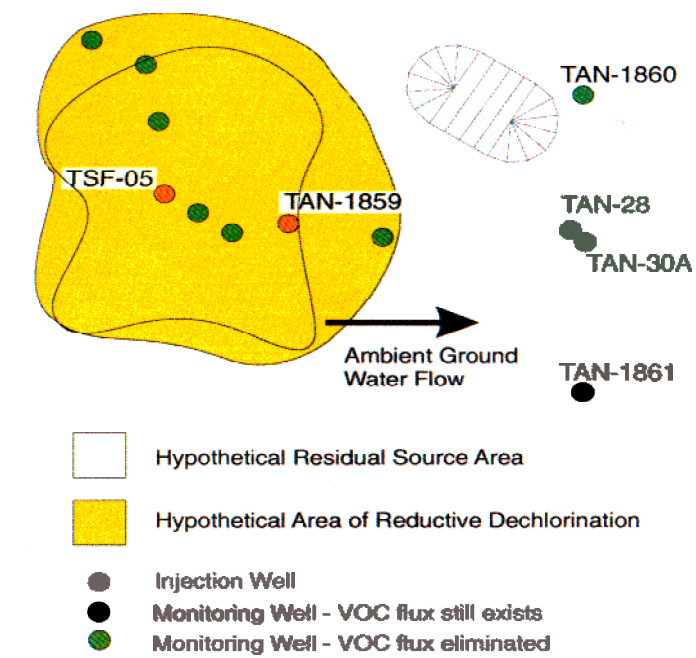


Figure 4-6. Dual injection points expected to increase area of active biodegradation to encompass source and eliminate both downgradient and crossgradient flux.

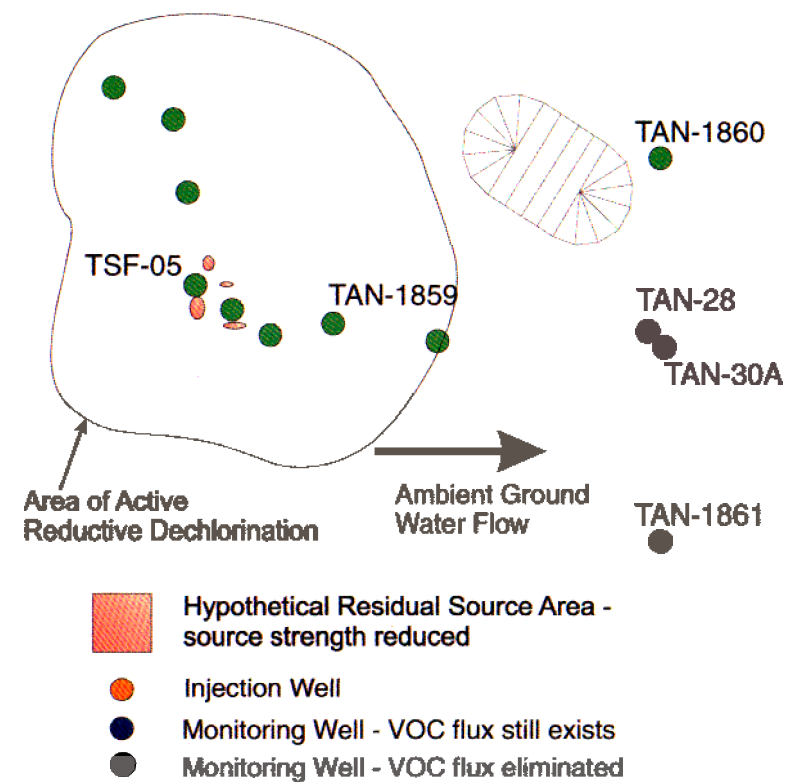


Figure 4-7. Maintaining sufficiently large biologically active zone will result in source degradation.

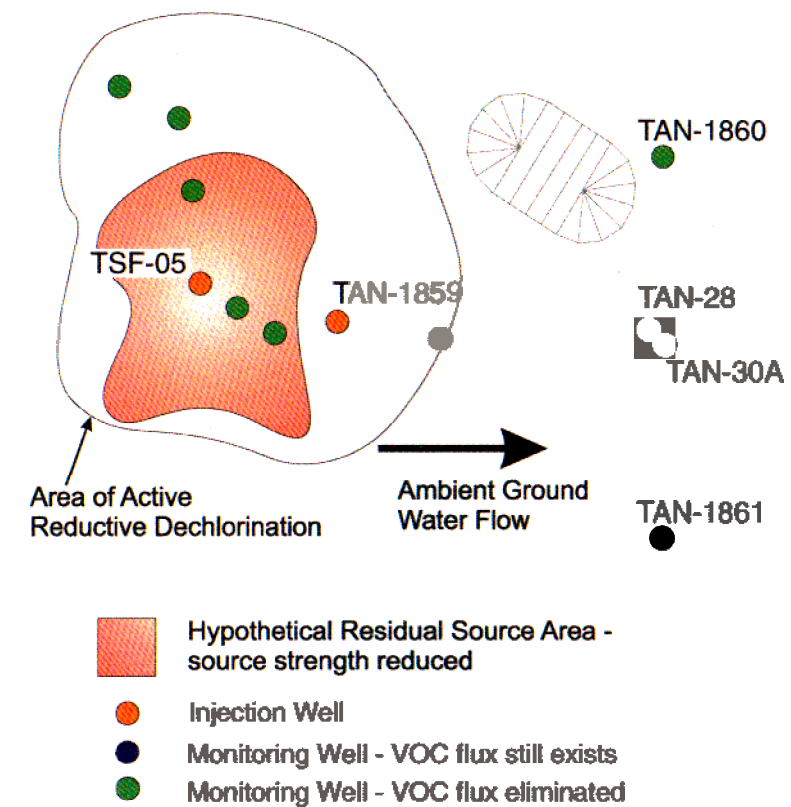


Figure 4-8. Residual source is degraded such that small pockets may remain, but volatile organic compound loading to groundwater is expected to be minimal.

Furthermore, the 1X 6% injections have resulted in sulfate concentrations rebounding to near background levels and ferrous iron and methane concentrations decreasing (see Section 3.1.2.2 and Figures 3-14, 3-18, and 3-22). The increased flux of reduced water resulting from the 4X 3% injections optimized conditions for ARD and allowed a biologically active zone that encompassed the residual source near TAN-D2 to cut off flux to and from this location. It appears that this "zone" was maintained for a sufficient time to degrade the source material near TAN-D2 because VOCs at TAN-D2 have not rebounded since the 4X 3% injections were replaced with 1X 6% injections and remain below MCLs. This trend is not only supported by the last two data points during this reporting period but continues to the present time (January 2004). The data will be discussed further in future reports.

#### 4.4 TAN-28 Rebound

As noted in the radiological results discussion in Section 3.4, tritium concentrations were found to be declining at a rate approximately equivalent to that of radioactive decay, except at TAN-28. Tritium concentrations at TAN-28 (see Figure 4-9) increased markedly in the spring of 2001 and have remained fairly constant since that time with an average concentration that is about 500 pCi/L greater than what it had been prior to that time. Interestingly, the tritium step increase was matched by increases in TCE, cis-DCE, and trans-DCE concentrations over roughly the same time period. This change does not appear to be in response to any particular change in injection strategy but rather follows the shutdown of the Air Stripper Treatment Unit (ASTU). The ASTU may have drawn less contaminated water into the vicinity of TAN-28, which served to dilute the concentrations until the ASTU was shut off. Volatile organic compound and tritium concentrations at TAN-29 and TAN-27 showed similar responses after the shut down of the ASTU.

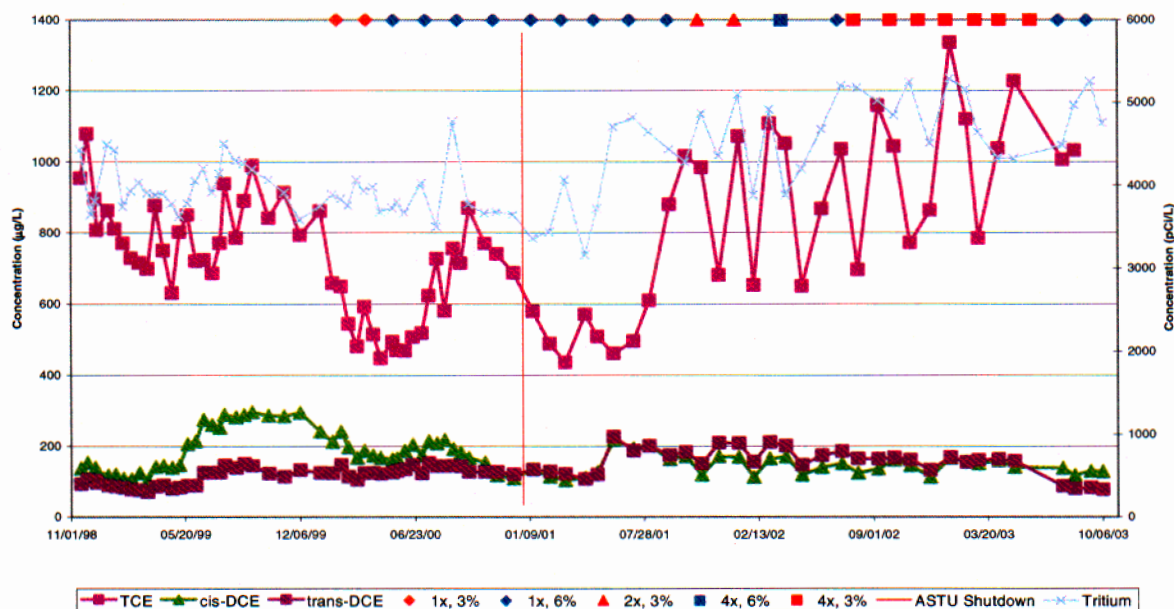


Figure 4-9<sup>c</sup>. Concentration changes at TAN-28 in relation to the shutdown of the Air Stripper Treatment Unit.

c. Note that the TCE data in this exclude two data points (79 and 5 µg/L from samples collected on May 5, 2003, and September 15, 2003) that are considered anomalous, as reported in Section 3.1.5.3.

## 4.5 Effect of Injection on Radionuclide Migration

As reported in Section 3, Sr-90 concentrations have exhibited some variability. Prior to ISB injections, concentrations at TAN-29 were in the range of 20 to 30 pCi/L. During the most recent reporting period, concentrations started at 50 pCi/L, dropped temporarily to nondetect, and then returned to the 50 to 60 pCi/L range. It is undetermined whether the observed changes are a result of natural variability in the hydrogeologic system or are effects from the injections of sodium lactate at TSF-05. Researchers previously investigated the potential for radionuclide migration from the source area and concluded that while radionuclides are likely to be mobilized within the ISB treatment area, downgradient effects would be minimal (DOE-ID 2002a). The following analysis is offered to provide a point of reference against which the TAN-29 Sr-90 concentrations can be compared.

Historical Sr-90 data provide evidence of rapid attenuation resulting from radioactive decay, precipitation, and sorption as the contaminant passes through the aquifer matrix. The observed attenuation rate can be utilized to estimate a maximum concentration ( $c_{\max}$ ) of Sr-90 activity at well TAN-29 that would lead to Sr-90 activity at well TAN-40 in excess of the MCL of 8 pCi/L. Sr-90 data from selected wells near TSF-05 were correlated with distance downgradient of TSF-05 by Starr (1999). Taking advantage of additional data collected up through this reporting period, Sr-90 activity can be described as a function of distance downgradient of TSF-05. Figure 4-10 shows a plot of the log transformed Sr-90 activity data against the linear distance along the approximate plume axis. The data are fit well by a linear regression. Lines corresponding to the upper and lower 95% confidence intervals on the regression are also illustrated.

Assuming that the Sr-90 spatial attenuation rate downgradient of the ISB treatment area is the same as or greater than the spatial attenuation rate derived from measurements taken within the treatment area, the trend observed in Figure 4-10 can be extrapolated to the location of TAN-40, which is a New Pump and Treat Facility extraction well located 358 ft downgradient from TAN-29 (Starr 1999). To be conservative, the slope of the upper 95% confidence limit (-0.0031) is used in this analysis. Figure 4-11 indicates that, given the observed attenuation rate, Sr-90 concentrations at TAN-40 would not be expected to exceed the MCL unless concentrations at TAN-29 were consistently above 103 pCi/L. In comparison, the highest concentration reported at TAN-29 to date has been 56 pCi/L. The recent Sr-90 data support the conclusion that although Sr-90 concentrations at TAN-29 have increased since the start of the injections, radionuclide migration beyond the ISB treatment area is not being substantially affected. In the future, should concentrations at TAN-29 begin to regularly exceed 103 pCi/L, monitoring at additional locations should be considered.

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c. Note that the TCE data in this exclude two data points (79 and 5 µg/L from samples collected on May 5, 2003, and September 15, 2003) that are considered anomalous, as reported in Section 3.1.5.3.



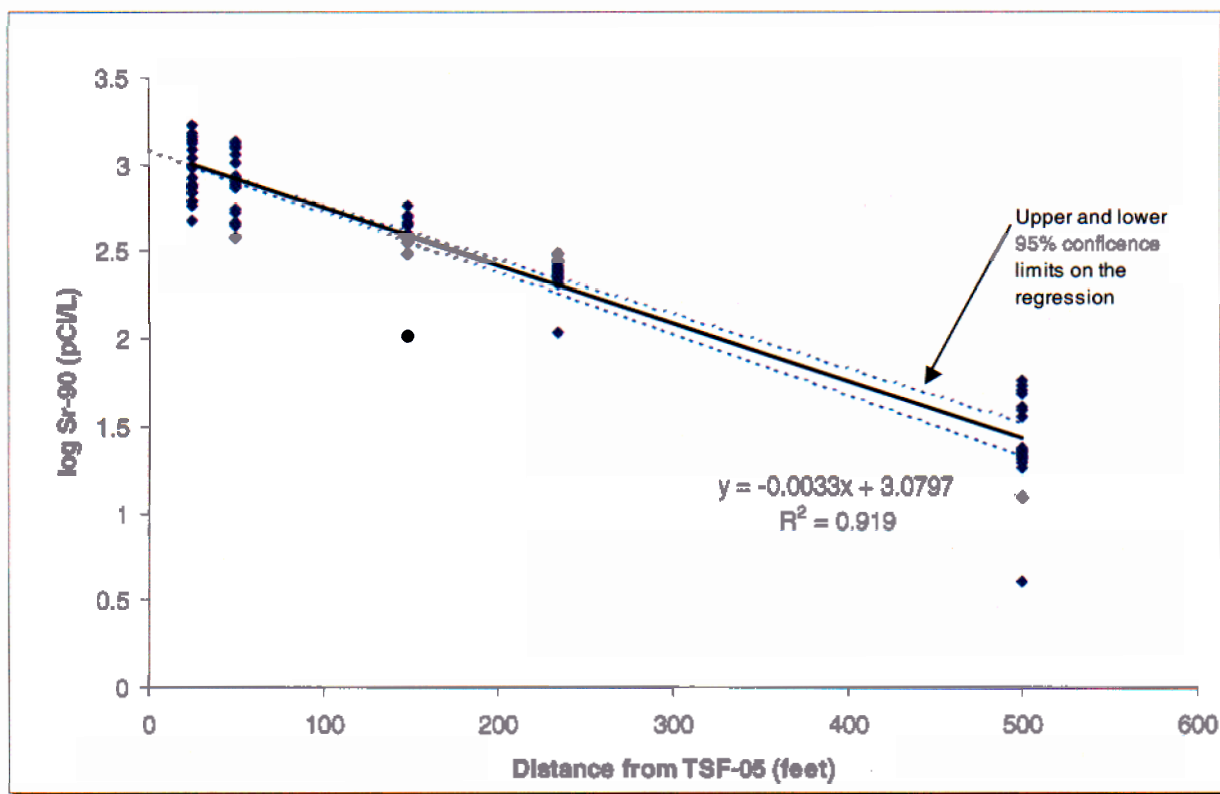


Figure 4-10. Historic Sr-90 activity data exhibiting a decreasing trend with distance from TSF-05.

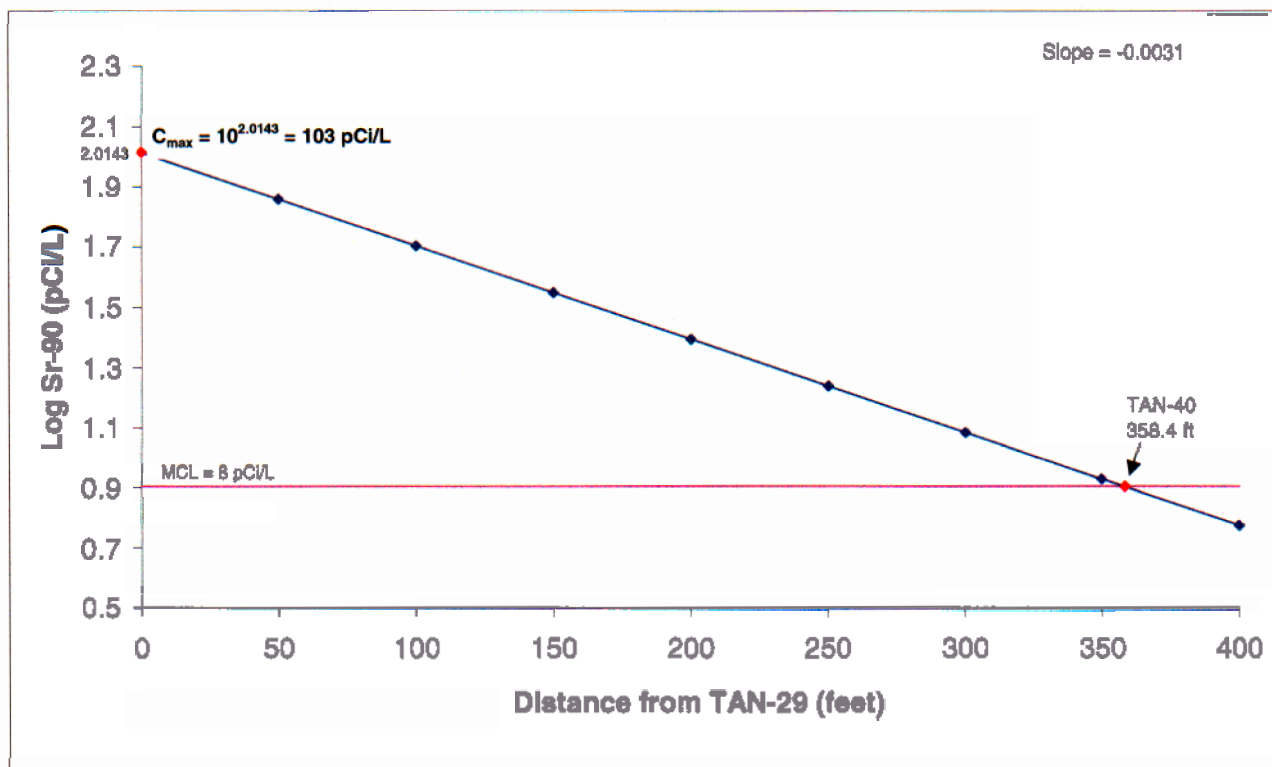


Figure 4-11. Extrapolation of the observed attenuation rate to downgradient well TAN-40.

## **4.6 Cost-Effectiveness of Monitoring Program**

Based on an evaluation of the data for this reporting period, the changes to the monitoring plan that were recommended in the previous annual report (INEEL 2003a) are still supported. Two additional changes may be considered to further reduce monitoring costs. First, in situ monitoring of water quality parameters during well purging is no longer necessary. Currently, purge parameters are recorded but are not used to adjust the purge rates or volumes. Because the ISB monitoring wells are already established and most are fitted with dedicated equipment, the purge rates and volumes specified in the procedures are demonstrated to be adequate. Therefore, there is little utility for the purge parameter data.

Second, the number of field and trip blanks collected can be reduced based on requirements of the Quality Assurance Project Plan (DOE-ID 2002c). Because the majority of the samples collected for performance monitoring of the ISB treatment are for nondefinitive, screening level data, any potential blank contamination resulting from airborne contaminants and equipment contamination would not significantly affect interpretation of ISB performance. It should also be noted that over the past 4 years of monthly sampling, field blank contamination has not been a quality issue. Therefore, the QA requirements in the GWMP (INEEL 2003b) could be revised so that preparation of field blanks and trip blanks would correspond with the collection of definitive confirmation samples for VOCs (semiannually). Field blanks should be analyzed for VOCs and tritium only. Likewise, trip blanks should be prepared for VOC analysis only.

## 5. CONCLUSIONS

In general, the ISB system continued to operate through the end of the Interim Operations Phase, stimulating ARD throughout most of the source area. Ethene was present in significant concentrations in all the source area wells, indicating active ARD. During this reporting period (November 2002 through October 2003), two injection strategies were tested. The first, 4X 3%, resulted in increased radial distribution of electron donor and increased ARD at locations near the edge of the source. TAN-D2, for example, is now “clean,” with all contaminants below MCLs. The VOC and redox data from TAN-D2 provide strong evidence that the residual source has been degraded near TAN-D2. However, the high volumes of potable water associated with the 4X 3% injections are thought to have reduced ARD efficiency, particularly in areas nearest the injection point. In July 2003, the injections were changed back to 1X 6%, which appear to be restoring efficiencies in the source area as TCE and cis-DCE concentrations are trending downward in the source area wells.

The ISB injection facility was also completed during this reporting period allowing injection into three wells as needed. Three new wells were also installed during this time (TAN-1859, TAN-1860, and TAN-1861). TAN-1859 was completed within the radius of the source sludge. TAN-1860 and TAN-1861 were completed outside of the source sludge. It is anticipated that TAN-1859 will initially be used as an injection well. All three wells provide additional monitoring locations near the downgradient edge of the source area. The completion of these activities allows the project to conclude Interim Operations and proceed into Initial Operations in accordance with the RAWP (DOE-ID 2002a).

The next two phases of ISB operations are Initial Operations and Optimization Operations, as described in Section 1.3. The goal of these phases is to eliminate flux of contaminants from the source area to downgradient and crossgradient locations. It is expected that continued testing of injection strategies, using single and dual well injection points, will result in additional progress toward this objective. Continued monitoring of the ISB wells will provide data to determine how effectively the injection strategies encompasses the entire source area, sustain efficient ARD conditions, and arrest flux of contaminants from the residual source.



## **6. RECOMMENDATIONS**

Based on the results of the 2003 ISB performance data, the following changes are recommended for Initial Operations:

- Test alternative injection strategies utilizing the available injection wells (TSF-05, TAN-31, and TAN-1859). Implement a phased approach whereby hydraulic response to each injection strategy can be monitored. Injections at various depths may also be considered for testing.
- Conduct an AED pilot test involving small-scale injections in TSF-05 and monitoring in TAN-25 and TAN-31.
- Continue the monthly PE sample program for VOC analysis conducted at the IRC laboratory. Also include PE samples with each shipment of VOC samples submitted to off-Site laboratories to provide more meaningful comparison between the SPME and 8260B methods (EPA 1996a).
- Eliminate monitoring of water quality parameters during well purging.
- Revise the GWMP (INEEL 2003b) to require preparation of field blanks and trip blanks only when definitive confirmation samples are collected (semiannually). Field blanks should be analyzed for VOCs and tritium. Trip blanks should be analyzed for VOCs only.





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